

Quantum Mechanics of a Simulated Trihydrogen Dication

ML Glasser

Departamento de Física Teórica, Atómica y Óptica,
Universidad de Valladolid 47071 Valladolid, Spain
Department of Physics, Clarkson University,
Potsdam, NY 13699-5820 (USA)

Abstract

The Schroedinger equation is solved exactly within the Born-Oppenheimer approximation for a simulacrum of the H_3^{++} -ion. The ion is assumed to form an isosceles triangle and the ground state energy is obtained over its geometrical parameter space. No multi-center molecular integrations are required. We indicate how the approximation to the actual molecule can be improved systematically.

pacs 31.15.Ar; 02.70.Wz; 31.50.Bc

1 Introduction

The Trihydrogen cation H_3^+ was identified, by mass spectroscopy, in 1911 by J.J. Thomson[1]. Twelve years later Hogness and Lunn[2] found that it could be produced by the proton exchange $H_2^+ + H_2 \rightarrow H_3^+ + H$ and would readily lose an electron. Subsequently it was found that H_3^+ is present in interstellar clouds and is among the most abundant molecular species in the universe. This led to the question of the stability of the dication H_3^{++} , which has remained somewhat controversial to the present, though the consensus is that it is unstable.

The first quantum treatment was by Gordadse[3, 4] in (1935), who assumed the protons were fixed, equally spaced along a straight line or formed an equilateral triangle. He used the variational method, as have all subsequent studies, based on a one-parameter trial function built from the hydrogen 1s-state. In spite of the simplicity of the trial functions, he found several of the multi-center integrations intractable, requiring not too well controlled approximations, and concluded that neither configuration was stable. About the same time C.A. Coulson carried out a LCMO study of H_3^{++} [5]. He used only a single molecular orbital and his energy values lie somewhat higher than those in [4]. The difficulty of these multi-center integrations have continued to dog such calculations and may be what prompted Eyring's comment that H_3^+ is "the scandal of modern chemistry" [6]. The first extensive study of H_3^{++} using electronic digital computers was by H. Conroy in 1964 [7,8,9,10], who devised an insightful set of variational wave functions and used Monte-Carlo algorithms for the integrations, remarking that "these integrations presented grave obstacles". This and subsequent calculations [11,12,13,14,15], mostly confined to the linear and

equilateral triangle configurations, have upheld Gordadse's conclusion that the ion is unstable. An attempt to produce the dication experimentally [16, 17] was unsuccessful.

The purpose of this note is to suggest that it is possible to avoid the variational method and consequent multi-center integrations entirely and that the Schroedinger equation can be solved exactly for a sequence of Hamiltonians that converge to the correct one. This note is intended as a proof of principle, and deals only with the first Hamiltonian in the sequence; it is equivalent to keeping only the hydrogen 1s state and is simple enough that most of the calculations can be done "by hand". We also assume that the ion forms an isosceles triangle and the ground-state energy (ignoring hyperfine effects) is examined as a function of a side and adjacent angle. Even so, the results lie reasonably close to the most recent values.

2 Hydrogen atom

Let the one-electron Hamiltonian of an atom (or indeed, any system) be

$$H = p^2 + V(\vec{r}) \quad (1.1)$$

and have bound-state eigenfunctions and energy levels $\{\phi_a, E_a\}$. Then, by completeness,

$$V(\vec{r}) = \sum_a v_a(\vec{r}) <\phi_a|, \quad v_a(\vec{r}) = V(\vec{r})|\phi_a >. \quad (1.2)$$

Thus, if we ignore the continuum states, which will be of no interest in the sequel, then we have a sequence of Hamiltonians

$$H_n = p^2 + \sum_{m=0}^n v_m <\phi_m| \quad (1.3)$$

and it is easily checked that the Schroedinger equation (we adopt units: $\hbar = 2m = e^2/2 = 1$)

$$\begin{aligned} \{-\nabla^2 - E\}\psi(\vec{r}) &= - \sum_{m=0}^n v_m(\vec{r})\lambda_m \\ \lambda_m &= \int d\vec{s} \phi_m^*(\vec{s})\psi(\vec{s}) \end{aligned} \quad (1.4)$$

has precisely the first n of the eigenstates of H . By transforming to momentum space and writing $E = -\epsilon < 0$ (since we are only concerned with bound states) (4) becomes the integral equation

$$\hat{\psi}(\vec{k}) = \sum_{m=0}^n \frac{\hat{v}_m(\vec{k})\lambda_m}{\epsilon + k^2}. \quad (1.5)$$

Next, by the Parseval relation for the Fourier transform [2] we have the consistency condition

$$\lambda_q = \frac{1}{(2\pi)^3} \int \hat{\phi}_q^*(\vec{k}) \hat{\psi}(\vec{k}) d\vec{k} = \sum_m A_{qm} \lambda_m$$

$$A_{qm} = \frac{1}{(2\pi)^3} \int \frac{\hat{v}_m(\vec{k}) \hat{\phi}_q^*(\vec{k})}{k^2 + \epsilon} d\vec{k}. \quad (1.6)$$

That is to say, the energy levels ϵ and corresponding λ 's are determined by the matrix equations

$$(\mathbf{A} - \mathbf{I})\Lambda = 0, \quad \text{Det}|\mathbf{A} - \mathbf{I}| = 0 \quad (1.7)$$

where Λ is the column vector $(\lambda_0, \dots, \lambda_n)^T$. In the next section we illustrate this by working out H_0 and H_1 for hydrogen.

It should be pointed out that in (1.2) the ϕ_a may be any complete set of functions, not just the eigenfunctions of H , though the low order approximations are unlikely to be as accurate.

2.1 Hydrogen atom

The lowest two bound-state wave functions for Hydrogen are[3]

$$\phi_0(r) = \pi^{-1/2} e^{-r}, \quad \epsilon_0 = 1, \quad \text{and} \quad \phi_1(r) = (32\pi)^{-1/2} (2-r) e^{-r/2}, \quad \epsilon_1 = \frac{1}{4}. \quad (2.1)$$

Hence,

$$\hat{\phi}_0(k) = \frac{8\sqrt{\pi}}{(k^2 + 1)^2}, \quad \hat{\phi}_1(k) = \frac{32\sqrt{2\pi}(4k^2 - 1)}{(4k^2 + 1)^3}$$

$$\hat{v}_0(k) = \frac{8\sqrt{\pi}}{(k^2 + 1)}, \quad \hat{v}_1(k) = \frac{8\sqrt{2\pi}(4k^2 - 1)}{(4k^2 + 1)^2} \quad (2.2)$$

and the matrix elements of \mathbf{A} are ($\epsilon = x^2$)

$$A_{00} = 2 \frac{3+x}{(1+x)^3}$$

$$A_{11} = 2 \frac{8x^3 + 20x^2 + 6x + 7}{(2x+1)^5} \quad (2.3)$$

$$A_{01} = \frac{32\sqrt{2}}{27} \frac{2x^2 + 5x - 7}{(1+x)(1+2x)^3}$$

$$A_{10} = \frac{8\sqrt{2}}{27} \frac{4x^2 + 12x - 7}{(1+x)^2(1+2x)^2}.$$

It is not difficult to check that the determinant in (1.7) has the form $(x-1)(2x-1)P(x)/Q(x)$ where P and Q are polynomials with positive coefficients, so its sole positive real roots are $x = 1/2$ and $x = 1$. The first equation (1.7) has the solution $\lambda_0 = 1$, $\lambda_1 = A_{10}/(1 - A_{00})$ and it is straightforward to check that inverting (1.5) with these values of x reproduces (2.1).

3 Triangular Molecule

Consider the three-proton system, in the Born-Oppenheimer approximation, where one lies at the origin and two lie in the $x - z$ -plane at positions

$$\vec{R}_{\pm} = R(\cos \alpha, 0, \pm \sin \alpha). \quad (3.1)$$

The Schroedinger equation for an electron subject to this configuration is

$$-(\nabla^2 + E)\psi(\vec{r}) = [V(\vec{r}) + V(\vec{r} - \vec{R}_+) + V(\vec{r} - \vec{R}_-)]\psi(\vec{r}). \quad (3.2)$$

Setting $E = -\epsilon$, (3.2) has the immediate solution in momentum space

$$\hat{\psi}(\vec{k}) = \frac{\hat{v}_0(\vec{k})}{k^2 + \epsilon} [\lambda_0 + e^{i\vec{k} \cdot \vec{R}_+} \lambda_+ + e^{i\vec{k} \cdot \vec{R}_-} \lambda_-] \quad (3.3)$$

with

$$\begin{aligned} \lambda_0 &= \frac{1}{(2\pi)^3} \int d\vec{k} \hat{\phi}_0(\vec{k})^* \hat{\psi}(\vec{k}) \\ \lambda_{\pm} &= \frac{1}{(2\pi)^3} \int d\vec{k} \hat{\phi}_0(\vec{k})^* e^{-i\vec{k} \cdot \vec{R}_{\pm}} \hat{\psi}(\vec{k}). \end{aligned} \quad (3.4)$$

Therefore, by defining the four integrals

$$\begin{aligned} I_0 &= \frac{1}{(2\pi)^3} \int d\vec{k} \frac{\hat{\phi}_0^*(\vec{k}) \hat{v}_0(\vec{k})}{k^2 + \epsilon} \\ I_{\pm} &= \frac{1}{(2\pi)^3} \int d\vec{k} \frac{\hat{\phi}_0^*(\vec{k}) \hat{v}_0(\vec{k})}{k^2 + \epsilon} e^{i\vec{k} \cdot \vec{R}_{\pm}} \\ I_1 &= \frac{1}{(2\pi)^3} \int d\vec{k} \frac{\hat{\phi}_0^*(\vec{k}) \hat{v}_0(\vec{k})}{k^2 + \epsilon} e^{-i\vec{k} \cdot (\vec{R}_+ - \vec{R}_-)}, \end{aligned} \quad (3.5)$$

we have the three consistency equations

$$\begin{aligned} \lambda_0 &= I_0 \lambda_0 + I_+ \lambda_+ + I_- \lambda_- \\ \lambda_+ &= I_+^* \lambda_0 + I_0 \lambda_+ + I_1 \lambda_- \\ \lambda_- &= I_- \lambda_0 + I_1^* \lambda_+ + I_0 \lambda_- \end{aligned} \quad (3.6)$$

The four integrals (3.5) are real, $I_+ = I_-$ and is independent of α . From (3.6) we see that the ground state energy ϵ is fixed by the determinantal equation ($\epsilon = x^2$)

$$F[R, \epsilon] \equiv (I_0 - I_1 - 1)[(I_0 - 1)^2 + (I_0 - 1)I_1 - 2I_+^2] = 0. \quad (3.7)$$

The integrals (3.5) are elementary:

$$I_0 = \frac{2(3+x)}{(1+x)^3}$$

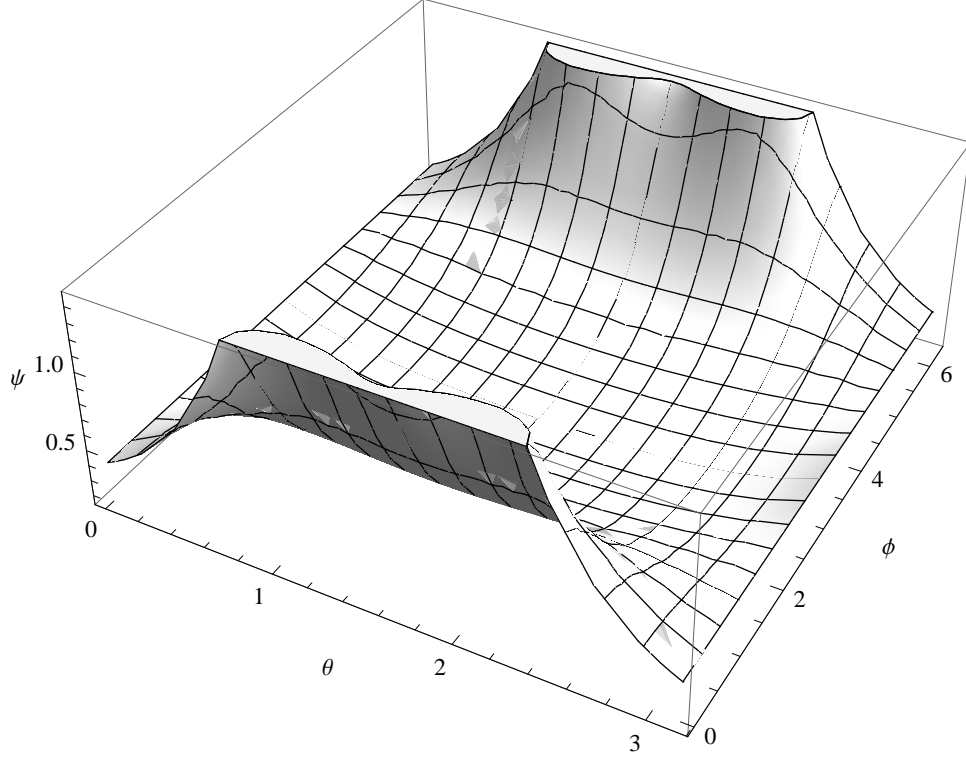


Figure 1: $\psi(1.6, \theta, \phi)$ for $0 < \theta < \pi$, $0 < \phi < 2\pi$.

$$I_{\pm} = f(R, x) = \frac{16}{(x^2 - 1)^2} \left\{ \frac{e^{-R} - e^{-Rx}}{R(x^2 - 1)} + \frac{1}{8} e^{-R} [x^2 - 5 + R(x^2 - 1)] \right\} \quad (3.8)$$

$$I_1 = f(2R \sin \alpha, x).$$

The spatial wave function is obtained through the Fourier inversion of (3.3) by which we find in spherical coordinates

$$\psi(r, \theta, \phi) = N \left\{ \frac{e^{-r} - e^{-xr}}{r} + \left(\frac{1 - I_0}{2I_+} \right) \left[\frac{e^{-\rho_+} - e^{-x\rho_+}}{\rho_+} + \frac{e^{-\rho_-} - e^{-x\rho_-}}{\rho_-} \right] \right\}, \quad (3.9)$$

where N is a normalization factor and

$$\rho_{\pm} = \sqrt{r^2 + r^2 - 2rR(\sin \theta \cos \varphi \cos \alpha \pm \cos \theta \sin \alpha)}. \quad (3.10)$$

The wave function in the equilateral triangle configuration for $r = R = 1.6$, is shown as a function of θ and φ in Fig.1.

4 Results and discussion

The ground state energy $E = -\epsilon = -x^2$ is given by the largest positive root x of (3.7) which is that of the second factor. This is most easily determined graphically and the results for four cases are given below.

4.1 Linear configuration: $\alpha = \pi/2$.

R	x	R	x
0	2.1349367	1.2	1.8036179
0.1	2.1307780	1.4	1.7347596
0.2	2.1187612	1.6	1.6694538
0.3	2.0999631	1.8	1.6082098
0.4	2.0756736	2.0	1.5512046
0.5	2.0471617	2.2	1.4984244
0.6	2.0155626	2.4	1.4497481
0.7	1.9818363	2.6	1.4049973
0.8	1.9467667	2.8	1.3639650
1.0	1.8749557	3.0	1.3264326

The ground-state energy vs R for $\alpha = \pi/2$ is shown in Fig.2 and the total molecular energy in Fig.3; the ion is unstable.

4.2 Equilateral triangle $\alpha = \pi/6$

R	x	R	x
0.0	2.1349367	1.2	1.9095172
0.1	2.1328424	1.4	1.8497556
0.2	2.1266444	1.6	1.7893258
0.3	2.1165658	1.8	1.7294701
0.4	2.1029191	2.0	1.6711139
0.5	2.0860668	2.2	1.6149246
0.6	2.0663935	2.4	1.5613632
0.7	2.0442855	2.6	1.5107287
0.8	2.0201173	2.8	1.4631940
1.0	1.9669892	3.0	1.4188350

The ground-state and total energies are shown as functions of R in Fig.2 and Fig.3 For this geometry with $R = 1.68$ the exact ground-state energy $x = 1.95426$ has been proposed[15]. Our value at this spacing is $x = 1.76526$ a difference of just under 10%. In Fig.4. we show our result for the total energy Et compared to a recent study of the equilateral case by Medel-Cobaxin et al.[18]

4.3 Isocles cases: $\alpha = \pi/3, \pi/8$

For completeness we show the total molecular energy for an obtuse ($\alpha = \pi/3$) and an acute ($\alpha = \pi/8$) triangular configuration in Figs.2-3. Again, in neither

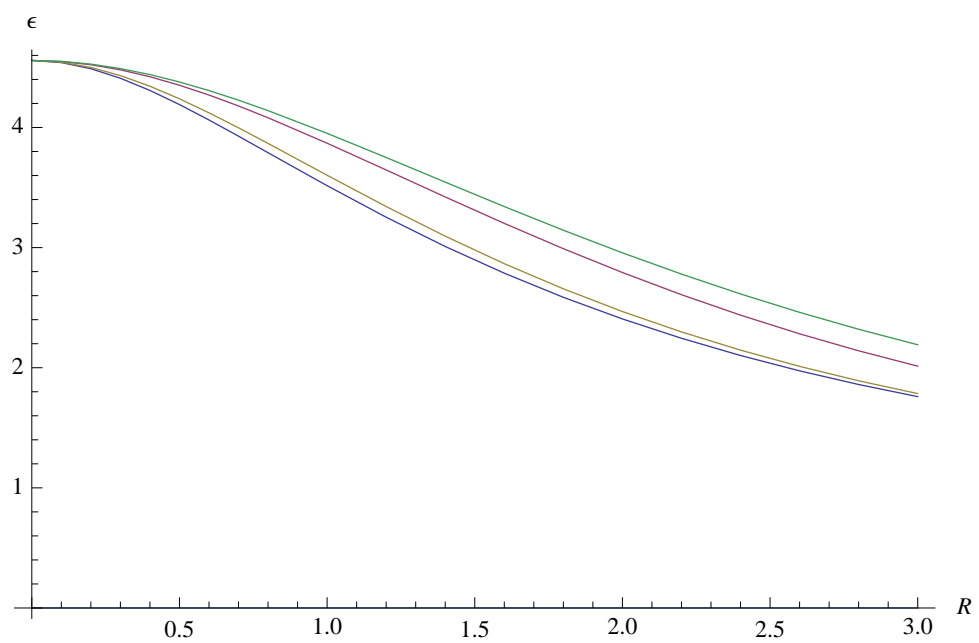


Figure 2: Ground-State energy ϵ vs R . From top to bottom at $R = 1$: $\alpha = \pi/8$, $\alpha = \pi/6$, $\alpha = \pi/3$, $\alpha = \pi/2$

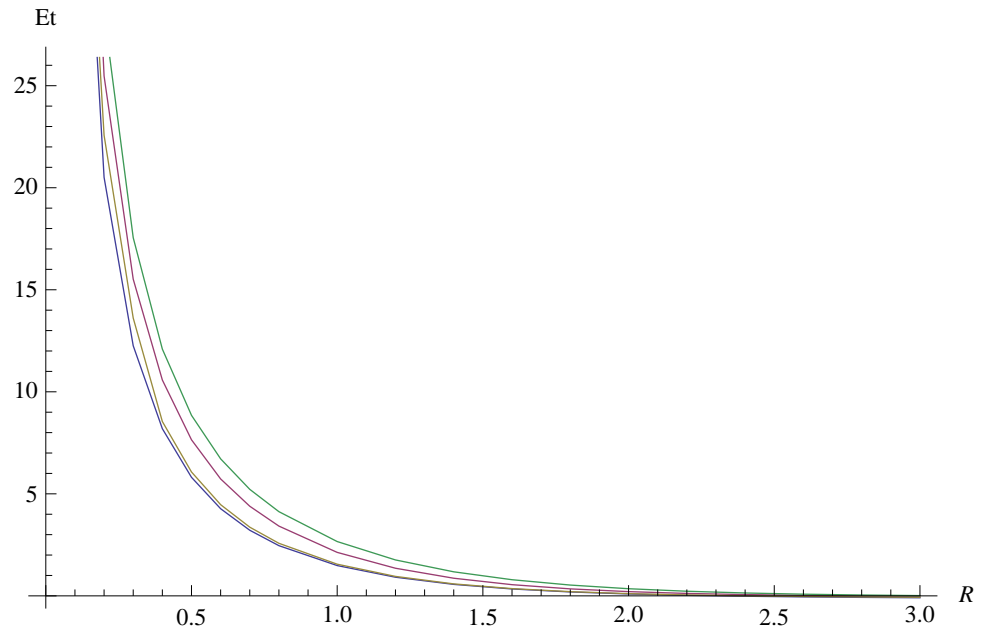


Figure 3: Total energy vs. R : Same order as in Fig.1.

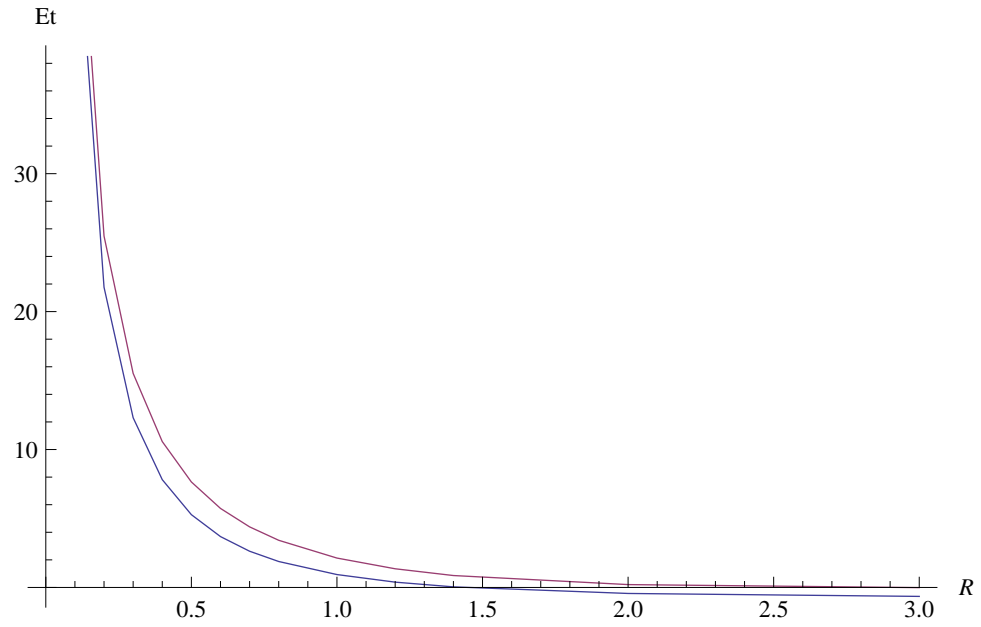


Figure 4: Total energy vs R : Comparison with Ref.[18]. Upper curve—this work.

case is the ion stable.

$$\alpha = \pi/3$$

R	x	R	x
0.0	2.1349367	1.2	1.8281244
0.1	2.1314613	1.4	1.7592914
0.2	2.1213259	1.6	1.6929713
0.3	2.1052384	1.8	1.6300407
0.4	2.0840921	2.0	1.5709739
0.5	2.0588167	2.2	1.5159789
0.6	2.0302939	2.4	1.4650897
0.7	1.9993156	2.6	1.4182289
0.8	1.9665685	2.8	1.3752500
1.0	1.8979968	3.0	1.3359649

$$\alpha = \pi/8$$

R	x	R	x
0.0	2.1349367	1.2	1.9365603
0.1	2.1331309	1.4	1.8828383
0.2	2.1277809	1.6	1.8280552
0.3	2.1190636	1.8	1.7733225
0.4	2.1072292	2.0	1.7194870
0.5	2.0925704	2.2	1.6671775
0.6	2.0754001	2.4	1.6168452
0.7	2.0560355	2.6	1.5688001
0.8	2.0347866	2.8	1.5232405
1.0	1.9877994	3.0	1.4802771

In conclusion, we have given the *exact* solution of the Schroedinger equation, within the Born-Oppenheimer approximation, for a model three-center molecule closely resembling H_3^{++} . For the equilateral configuration, where an exact ground-state energy at $R = 1.68$ has been proposed[15] the value calculated here agrees to better than 10%.. Furthermore, for our model:

- No multi-center molecular integrals are required.
- The approximation can be systematically improved.
- The corresponding Dirac equation can be solved exactly [20].
- Electric and magnetic fields can be included requiring only the solution of a first or second order ODE.[21]
- It may be feasible to treat the Kohn-Sham equations on the same basis, in which case correlation effects can be included.

Acknowledgements

I thank the Universidad de Valladolid, Valladolid, Spain and the DHIP, San Sebastian, Spain, where this work was carried out, for their hospitality. I am also grateful to Prof. Carlos Balbas for comments and references.

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